Organic Combustion in the Presence of Ca-Carbonate and Mg-Perchlorate: A Possible Source for the Low Temperature CO2 release seen in Mars Phoenix Thermal and Evolved Gas Analyzer Data

Two of the most important discoveries of the Phoenix Lander were the detection of ~0.6% perchlorate [1] and 3-5% carbonate [2] in landing site soils. The Thermal and Evolved Gas Analyzer (TEGA) instrument on the Phoenix lander could heat samples up to ~1000 °C and monitor evolved gases with a mass spectrometer. TEGA detected a low (~350 °C) and high (~750 °C) temperature CO2 release. The high temp release was attributed to the thermal decomposition of Ca-carbonate (calcite). The low temperature CO2 release could be due to desorption of CO_2, decomposition of a different carbonate mineral, or the combustion of organic material. A new hypothesis has also been proposed that the low temperature CO2 release could be due to the early breakdown of calcite in the presence of the decomposition products of certain perchlorate salts [3]. We have investigated whether or not this new hypothesis is also compatible with organic combustion.

Magnesium perchlorate is stable as Mg(ClO4)2-6H2O on the martian surface [4]. During thermal decomposition, this perchlorate salt releases H2O, Cl2, and O2 gases. The Cl2 can react with water to form HCl which then reacts with calcite, releasing CO2 below the standard thermal decomposition temperature of calcite. However, when using concentrations of perchlorate and calcite similar to what was detected by Phoenix, the ratio of high:low temperature CO2 evolved is much larger in the lab, indicating that although this process might contribute to the low temp CO2 release, it cannot account for all of it.

While H2O and Cl2 cause calcite decomposition, the O2 evolved during perchlorate decomposition can lead to the combustion of any reduced carbon present in the sample [5]. We investigate the possible contribution of organic molecules to the low temperature CO2 release seen on Mars.

To perform these analyses, Iceland spar calcite (5%) and Mg(ClO4)2-6H2O (1%) are mixed into a corundum powder (94%) which had been heated to 1100 °C in air to remove any organic contaminants. This was the base material into which organics were added. Three different organic molecules were selected for this study: coronene, a polycyclic aromatic hydrocarbon (C24H12), naphthalene-1,4-dicarboxylic acid (C12H8O4), and mellitic acid (C12H6O12). These organics are consistent with meteoritically delivered organic material that has been oxidized to various levels by surface processes on Mars [6, 7].

Organics are mixed into the calcite-perchlorate-corundum material with a mortar and pestle to concentration of 1, 0.5, 0.1, and 0.05%. ~100 mg of sample is placed into a sample crucible and loaded into a Setaram Ligne 96 differential scanning calorimeter. Samples are heated up to 1350 °C at 20 °C/minute in a sample chamber at 12mbar pressure, using N2 as a carrier gas with a flow rate of 1sccm. The exhaust line of the DSC is connected to a Pfeiffer quadrupole mass spectrometer to measure the evolved gases. All samples are run at least twice and the results are checked for consistency.

The presence of organic molecules increases the amount of low temperature CO2 released, coincident with the early decomposition of calcite caused by perchlorate decomposition. However, the very high concentration of organics needed to match the TEGA data suggests that organics cannot be the sole source of the observed CO_2 released.

[1] Hecht M.H. et al. (2009) Science, 325, 64-67 (1997) JGR, 90, 1151–1154. [2] Boynton W.V. et al. (2009) Science, 325, 61-64. [3] Cannon K.M. et al., LPSC XLIII. [4] Besley L.M. and Bottomley G.A. (1969) J. Chem. Thermodyn, 1, 13-19. [5] Ming D.W. et al. (2009) LPS XL, Abstract #2241. [6] Benner S.A. et al. (2000) PNAS, 97, 2425-2430. [7] Pizzarello S. (2004) Origins Life Evol B, 34, 25-34.